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SAMPLING AND ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AND OXYGENATED PAH IN DIESEL EXHAUST AND AMBIENT AIR

Eva LEOTZ-GARTZIANDIA⁽¹⁾, Véronique TATRY⁽¹⁾ and Patrick
CARLIER⁽²⁾

(1)INERIS (Institut National de l'Environnement Industriel et des Risques)
Parc Technologique Alata, B.P. 2, 60550 Verneuil-en-Halatte, France

(2)LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques)
Univeristé Paris XII, 61 avenue du Général de Gaulle, 94010 Créteil cedex,
France

Abstract. Polycyclic Aromatic Hydrocarbons (PAH) and their oxygenated derivatives occur in particles or in the vapour phase in the atmosphere. Some of these compounds, particularly the PAH, are known as strong carcinogens and/or mutagens. Emissions from diesel engines are an important source of these contaminants in urban air. In this work, the chemical composition of diesel particles was studied from two different perspectives: the gaz/particule partitioning and the different size fractions of these compounds. A dilution tunnel, with a diesel car connected, was built for the purpose of this study. Measurements were carried out near a motorway in Paris for comparison to the tunnel test results. The results show, firstly, that the gaseous phase of the PAH is predominant (up to 20 times) with respect to the particulate phase, and that the PAH and their derivatives are mainly adsorbed in the very fine particulate fraction (for particle size under 0.4 μm). Secondly, the oxygenated PAH, neglected in the majority of previous studies, are predominant with respect to the PAH.

Keywords : diesel emissions dilution chamber gas/particle partitioning
PAH oxygenated PAH

1. INTRODUCTION

Several epidemiological studies indicate that mortalities and morbidities can be correlated to the concentrations of atmospheric aerosols [1,2] and short term health effects (respiratory problems, asthma incidents...) have been reported too [3]. These problems are normally associated with very fine particles (diameter < 2 or $3\ \mu\text{m}$)

In urban air 50 to 80 % of fine particles come from traffic sources. In France, diesel engines account for 30 % of the total traffic. In 1995 the French motor industry estimated that 87 % of these particles came from diesel vehicles, 12 % came from gasoline vehicles without catalysed engines and 1 % came from vehicles with catalysed engines.

The Diesel exhaust is a complex mixture of gases, vapours and particulate matter that is the result of the incomplete combustion of diesel fuel and lubricants. In general 10 % to 40 % of the particle phase consists of organic compounds extractable by solvents. These extracts include PAH and many oxygenated PAH. Several of these compounds are found distributed between both the gaseous and particulate phases [4,5,6].

Diesel particles are very small (average diameter near $0.2\ \mu\text{m}$), they have a respirable size, and once they are inhaled, they can reach the pulmonary alveoli, carrying with them any adsorbed organic compounds. This can provoke respiratory problems as well as mutagenic or genotoxic effects. There is a wider knowledge of the toxicity of PAH e.g., BaP, than there is for oxygenated PAH, for which complete toxicological data is not yet available.

For a comprehensive assessment of the health risks of diesel emissions it is necessary to have a good understanding of their chemical identity, atmospheric concentrations, the distribution between the particulate and gaseous phases, and also their biological activity.

2. DIESEL PARTICLES

The particle phase of diesel emissions consists of aggregates of spherical carbonaceous particles (about $0.2\ \mu\text{m}$ in mass median aerodynamic diameter), upon which significant amounts of high-molecular-weight organic compounds are adsorbed when the hot engine exhaust cools down to ambient temperature (figure 1). The particles in

diesel emissions are unique, because they have large surface areas allowing the adsorption of organic compounds.

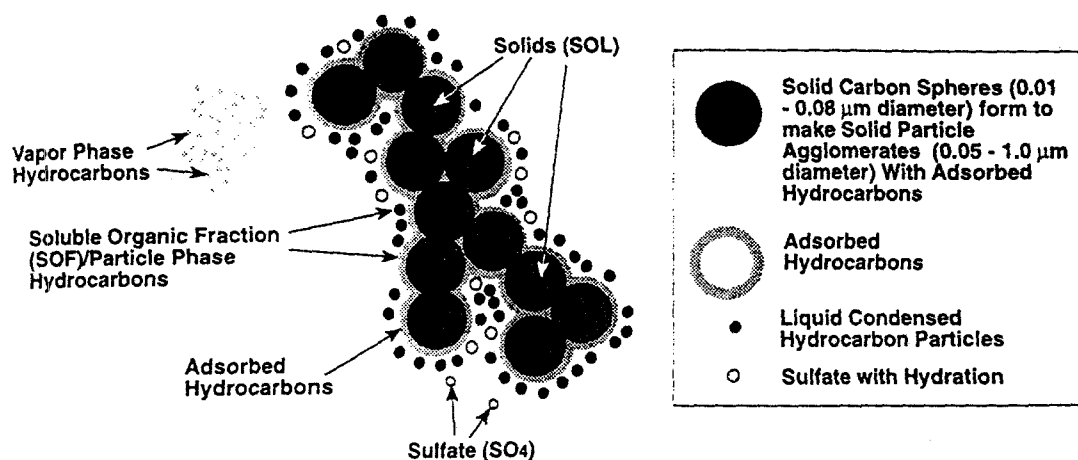


FIGURE 1. Schematic drawing of diesel particles and vapor-phase compounds (H.E.I., 1995)

10 to 40 % of the diesel particulate mass is normally due to organic compounds which include high-molecular-weight hydrocarbons and semi-volatile hydrocarbons.

The organic compounds present in diesel particles can be classified into three groups:

- aliphatic hydrocarbons: alkanes, alkenes ...
- aromatic hydrocarbons: polycyclic aromatic hydrocarbons (PAH)
- polar hydrocarbons: oxygenated and nitrated PAH, dicarboxylic acids, alcanoic acids...[7].

The distribution of these compounds between the gas and particle (adsorbed) phases depends on the physico-chemical properties, e.g. ambient temperature and humidity.

Diesel particles have been classified as “probably carcinogenic” in humans by the « Centre International de Recherche sur le Cancer (CIRC) » and the US EPA (Environmental Protection Agency) and several hydrocarbons present in these particles are or are suspected to be carcinogenic and/or mutagenic (e.g. BaP, BaA, DBahA, nitro-PY, fluorenone).

After inhalation these compounds can be absorbed by the organism and mutations in humans can be induced by them. Therefore, they could conceivably play a role in both genotoxic and non-genotoxic carcinogenesis[8,9].

Our work was focused on two aspects:

- characterization of organic compounds in the diesel particles in a dilution tunnel, both in the particle and the gas phases and in different size fractions, with special emphasis on oxygenated PAH.
- the collection of atmospheric particles during a test campaign in the neighbourhood of Porte d’Auteuil in Paris to compare their composition with the results obtained with the particles collected in the dilution tunnel experiments.

3. EXPERIMENTAL

3.1. Choice of the organic compounds.

They were chosen because they are known to be : molecular markers for diesel emissions, toxic or suspected toxic substances and photochemically active.

We chose:

- aromatic hydrocarbons : 17 HAP from EPA Method TO-13: NAP, ACE, AC, FLN, PHE, ANT, FL, PY, B(a)A, CHR, B(e)P, B(b)F, B(k)F, B(a)P, DB(ah)A, B(ghi)P, IP
- polar hydrocarbons : 1-napthaldehyde, fluorenone, anthraquinone, phenanthrene-9-carboxaldehyde

3.2. Sampling methods

Samples of diesel particles were collected by using two different apparatus :

- A High Volume Sampler (HVS) inspired on the PS-1 (General Metal Works Inc.) built in our laboratory. Particles were collected on a

10.16 cm diameter quartz fiber filter and the gas phase compounds were collected in two cylindrical plugs of polyurethane foam (PUF) located downstream of the filter. The flow rate was approximately 17 Nm³/h.

- And a 6-stage cascade impactor (Andersen) in order to separate particles according to their aerodynamic size. Quartz fiber filters were used. The different stages of the impactor were separated in four granulometrics groups to minimize the analytical work : > 4.2 µm (A), 1.3-4.2 µm (group B), 0.4-1.3 µm (group C) and <0.4 µm (group D or final stage). The flow rate was about 33 Nm³/h.

After air sampling the PUF and the filters were wrapped in aluminium foils and stored at 4 °C. They were always analysed within 48 h.

3.3. Analytical methods

All samples (filters and PUF) were Soxhlet extracted with dichloromethane for 24 hours. The extracts were concentrated under a current of nitrogen and transferred into hexane. The samples were cleaned up on a alumina-silicagel column containing 1 g alumina (5 % water) and 1 g silicagel (5 % water). 1 ml of hexane containing the extract was added to the top of the column and the PAH were eluted with 4 ml of dichloromethane:hexane (20:80) mixture and the oxygenated PAH were eluted with 4 ml of methanol:dichloromethane (20:80) mixture.

The PAH were analyzed using a HPLC with fluorescence/UV detection and GC-MS apparatus. The oxygenated PAH were analyzed using a GC-FID and GC-MS apparatus.

Quantification was performed from the GC and HPLC profiles using representative hydrocarbons as external standards. Recovery rates of the analytical method and blanks were calculated for all the hydrocarbons studied and the results were corrected according to them.

The detection limit was 1 ng/m³ for the oxygenated PAH and 0.01 ng/m³ for the PAH [10].

4. THE DILUTION TUNNEL

We built a dilution tunnel which was connected to a diesel car. With this tunnel it was possible:

- to use a standard car

- to efficiently dilute the exhaust gases and to obtain an homogeneous mixture between exhaust gases and ambient air (which is filtered later on).
- to reproduce the chemical and physical phenomena (like reactions, and the adsorption of the compounds on the particles)
- to monitor temperature, humidity and compounds like NO_x and CO_2
- to connect the HVS and the impactor

Stainless steel was used for the tunnel and quartz wool permitted thermal insulation (figure 3).

The flow in the tunnel was optimised for the different samplers to allow collection under isokinetic conditions. $154 \text{ Nm}^3/\text{h}$ and $126 \text{ Nm}^3/\text{h}$ for the HVS and the impactor, respectively.

Blank runs were carried out in the air dilution with the two apparatus. For oxygenated PAH the results were under detection limits. For PAH, the results for NAP, FL and PHE were between 1 and 6 ng/m^3 and for the others they were under detection limits.

5. RESULTS AND DISCUSSION

5.1.Characterization of organic composition of diesel particles

For this study The « Institut Français du Pétrole, IFP » supplied a car and a reference fuel. Real time determinations of temperature, humidity, carbon dioxide (CO_2) and oxides of nitrogen (NO_x) were carried out in the dilution tunnel. Each sample was obtained during 5 minutes at 30°C with the HVS and the impactor and each experiment was carried out three times. A good repeatability of the experiments was observed.

All the organic compounds studied were found in the diesel exhaust (gas and particulate). The n-alkanes and a complex mixture of branched and cyclic hydrocarbons was found in each sample.

Table 1 show the concentrations of PAH in gas and particle phases. PHE, FL and PY were the major constituent, these compounds are characteristic molecular markers for diesel exhaust components [11]. The concentration of NAP in the gas phase was high.

	Particle (ng/m3)	Gas (ng/m3)
NAP	0.26	149.19
ACE	0.00	11.18
AC	0.00	7.25
FLN	0.18	13.79
PHE	2.14	36.47
ANT	0.30	12.07
FL	0.10	7.86
PY	0.93	3.81
B(a)A	0.32	0.60
CHR	0.11	0.40
B(e)P	0.04	0.00
B(b)F	0.04	0.06
B(k)F	0.02	0.00
B(a)P	0.04	0.00
DB(ah)A	0.03	0.00
B(ghi)P	0.06	0.00
IP	0.04	0.00

TABLE 1. Concentration of the gaseous and particulate phases of PAH in diesel exhaust (the mean of three values).

In the three experiments the gaseous fraction was predominant with respect to the particulate phase (Figure 2). Up to 15 times more predominant for the PAH between FLN and FL. The importance of sampling the gas phase was demonstrated.

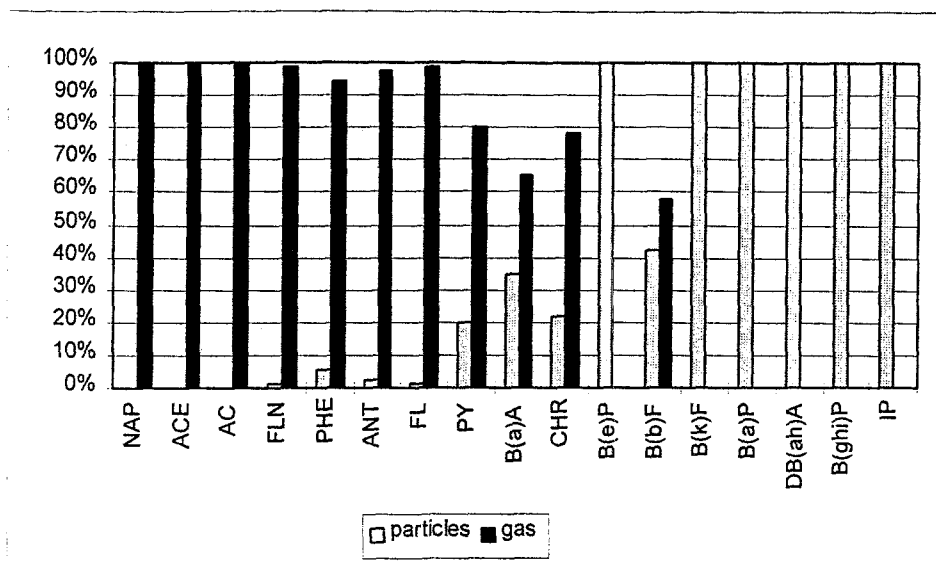


FIGURE 2. The percentage distribution of each PAH between the gas and particle phases.

4 series of diagnostic PAH ratios were defined (the particle phase was only used) for comparison with the ones corresponding to diesel source inputs [12,13]. In Table 2 a good correlation with the available data in the previous studies is shown.

	Filter 1	Filter 2	Filter 3	Diesel [12,13]	Gasoline [12,13]
PHE/(PHE+ANT)	0.87	0.88	0.88	-	0.77
FL/(FL+PY)	0.1	0	0.16	-	0.43
BeP/(BeP+BaP)	0.59	0.46	0.5	0.44	0.53
IP/(IP+BghiP)	0.44	0.39	0.44	0.46	0.18

TABLE 2. Source inputs correlation ratios for this study and the previous studies.

The results obtained for the oxygenated PAH are shown in Figure 3, for both the gas and particulate phases. The naphtaldehyde

was the major component in the two phases. Contrary to what we saw for the PAH, the concentration of oxygenated PAH in the particle phase was greater than that of the gas phase. This is because the volatility of these compounds is less than that of the PAH.

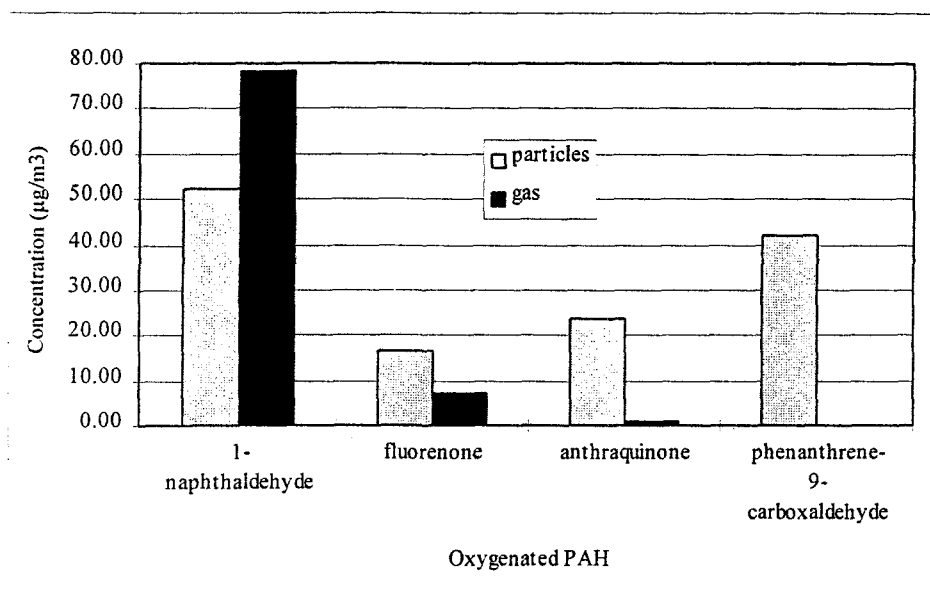


FIGURE 3. Concentration of the gaseous and particulate phases of the oxygenated PAH in diesel exhaust (the mean of three values).

The results obtained showed that there is a bigger proportion of oxygenated PAH than PAH in the particulate phase. For the compounds studied, the sum of concentrations of the 4 oxygenated PAH was 30 times greater than the sum of the concentrations of the 17 PAH. This shows that the importance of these compounds has been underestimated as they have been neglected in the majority of previous studies.

The same PAH and oxygenated PAH were identified with the impactor. The concentration of oxygenated PAH was greater than that of PAH again, and the results obtained showed, that all the studied compounds (PAH and oxygenated PAH) are mainly found in the very fine particulate fraction (for particle size under 0.4 µm) Fig 4.

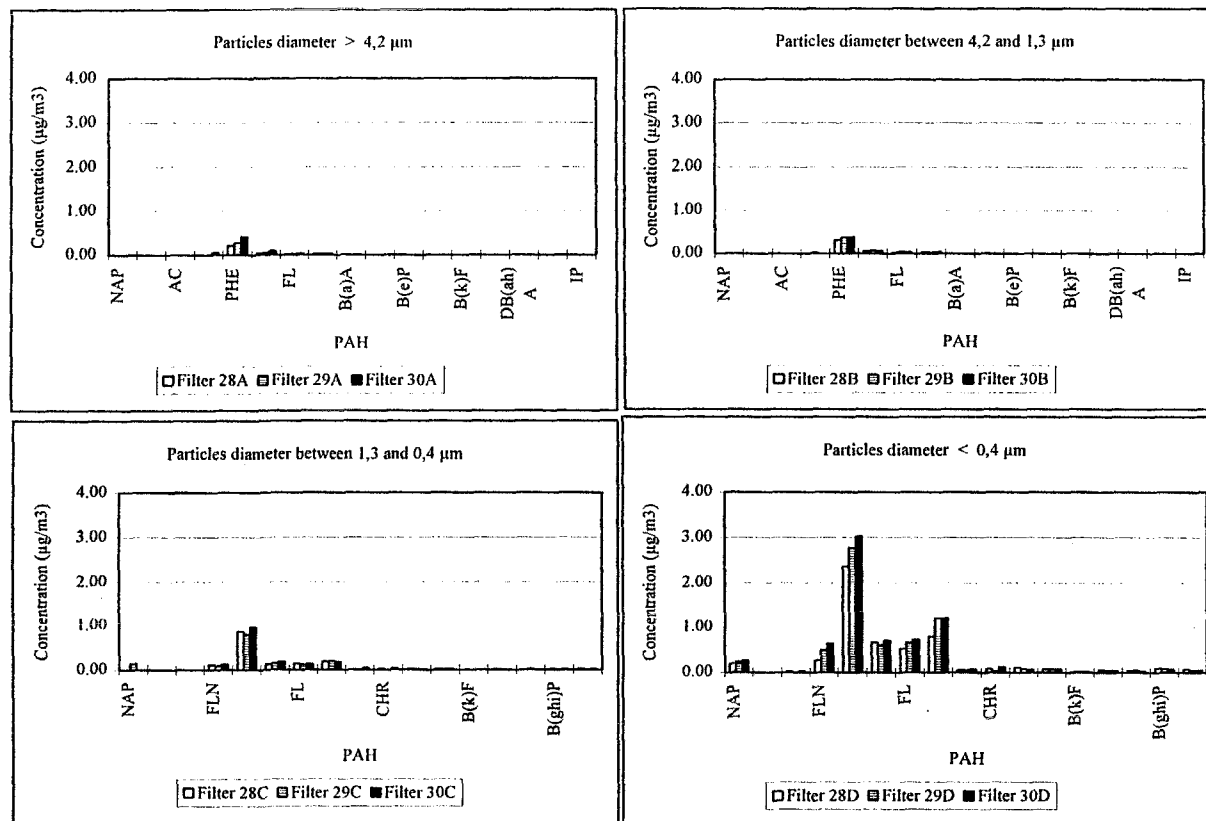


FIGURE 4. Concentration of PAH in the different size partitions in diesel exhaust.

This fraction can reach the pulmonary alveoli, which enhances the risk of introducing the organic compounds, present in these particles, into the organism.

Table 2 summarises the toxicological data of studied compounds [14].

PAH	Toxicity	Carcinogenicity	Mutagenicity	Reported in
Naphtalène	Moderate	Not confirmed		EPA-TSCA
Acénaphthylène	Moderate		Established	EPA-TSCA
Acénaphthène	Moderate		Established	EPA-TSCA
Fluorène	Weak		Established	EPA-TSCA, IARC
Phénanthrène	Moderate		Established	EPA-TSCA, IARC
Anthracène	Moderate		Established	EPA-TSCA, IARC
Fluoranthène	Moderate	Not confirmed	Established *	EPA-TSCA, IARC
Pyrène	Moderate	Not confirmed	Established *	EPA-TSCA, IARC
Benzo(a)anthracène	Poison	Confirmed	Established *	EPA-TSCA, IARC
Chrysène		Confirmed	Established *	EPA-TSCA, IARC
Benzo(b)fluoranthène		Confirmed	Established	IARC
Benzo(k)fluoranthène		Confirmed	Established	IARC
Benzo(a)pyrène	Poison	Confirmed	Established *	EPA-TSCA, IARC
Benzo(e)pyrène		Not confirmed	Established *	IARC
Indeno(1,2,3-cd)pyrène		Confirmed	Established	EPA-TSCA, IARC
Benzo(g,h,i)pérylène		Not confirmed	Established	IARC
Dibenzo(a,h)anthracène	Poison	Confirmed	Established *	EPA-TSCA, IARC
1-naphthaldehyde	Moderate			EPA-TSCA
Fluorenone		Not confirmed		EPA-TSCA
Anthraquinone	Moderate		Established	EPA-TSCA

* Human mutagen

IARC : International Agency for Research on Cancer

EPA-TSCA : Environmental Protection Agency-Toxic Substances Control Act

TABLE 2. Toxicological data of PAH and Oxygenated PAH studied in this work [14]

Extensive toxicological data are available for PAH which is not the case for oxygenated PAH, particularly for phenanthrene-9-carboxaldehyde. A few toxicological data are available for them with respect to the evaluation of the air quality.

5.2. Paris campaign

To complete the tunnel dilution tests, measurements were carried out near a motorway for a week (Paris-Porte d'Auteuil). A HVS was used to collect the gas and particle phases for PAH and oxygenated PAH.

2 series of 12 h samplings (day and night) for 5 days were performed. The CO, NO, NO₂, traffic and carbon data were obtained during the same period. A good correlation between CO, NO, traffic and the PAH and oxygenated PAH maxima was observed, and the concentration of these compounds was high in the day samplers.

We systematically observed, a predominance of the gaseous fraction with respect to the particulate phase, up to 10 to 20 times more predominant for PAH between FLN and FL (Fig 5) and a higher concentration of oxygenated PAH than PAH in the particulate phase, by a factor of almost 10 (Fig 6). It is important to recall again that some of the oxygenated PAH family are mutagenic, but current toxicological knowledge is poor.

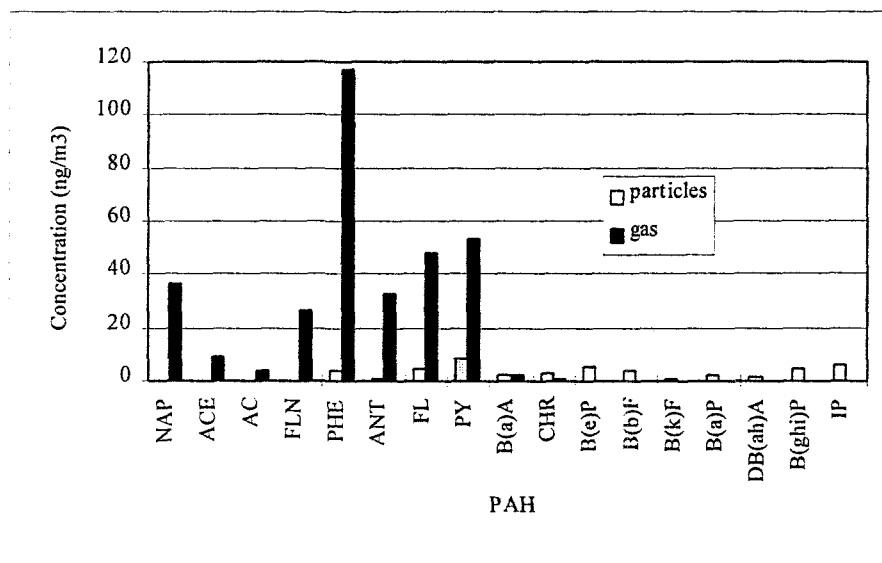


FIGURE 5. A day concentrations of PAH in Porte d'Auteuil (Paris)

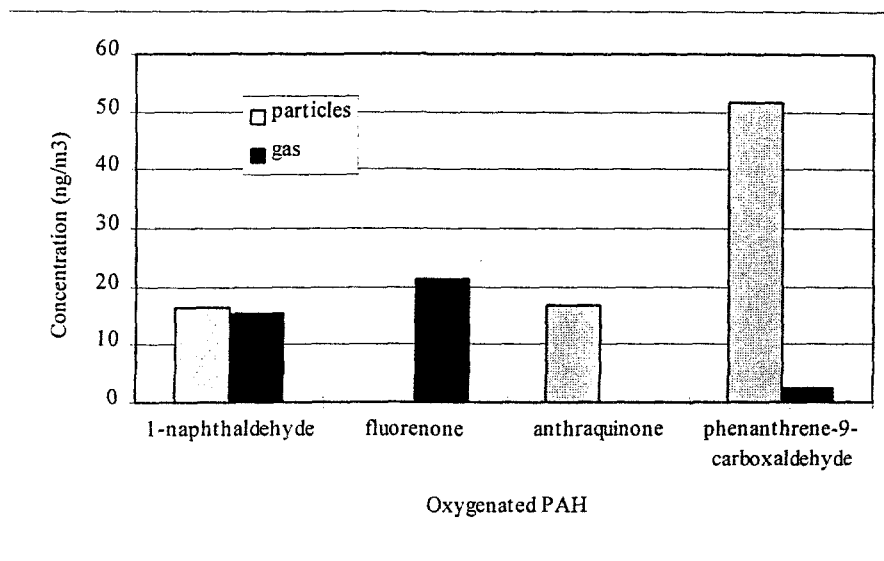


FIGURE 6. Concentration of the gaseous and particulat phases of oxygenated PAH at Porte d'Auteuil during the day.

We observed too the contribution of different sources of samples: vehicular emissions (diesel and gasoline) and natural emissions (measurements were carried out in spring near the « Bois de Boulogne »).

The percentage distribution of PAH in diesel as determined by the test results is shown in Fig 7 and they are compared to those previously found in gasoline [15].

Fig 8 shows the percentage distribution of these PAH found in the sampled particulate phase during the day-time sampling campaign at Paris.

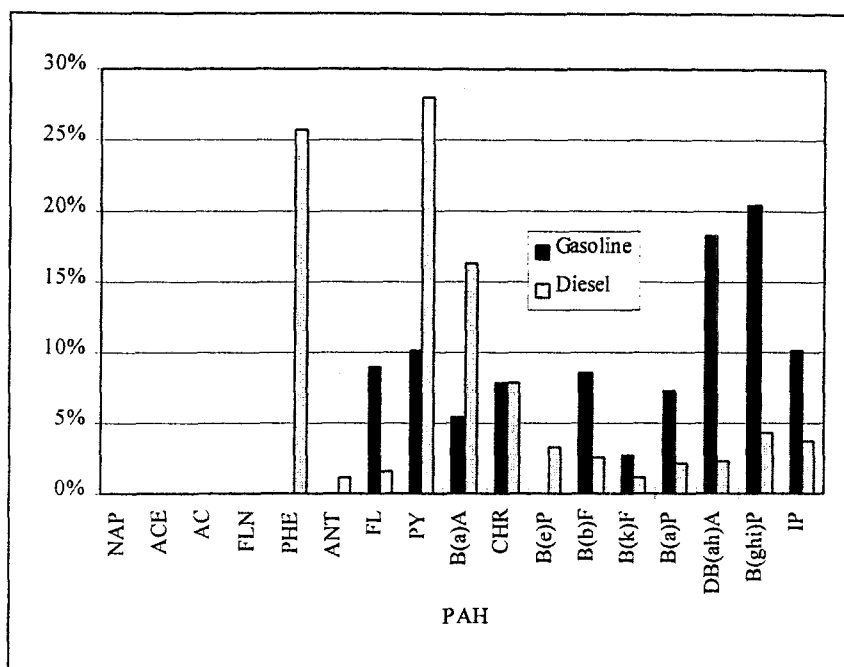


FIGURE 7. Comparison of diesel (results from the dilution tunnel) and gasoline (results from literature) PAH profiles

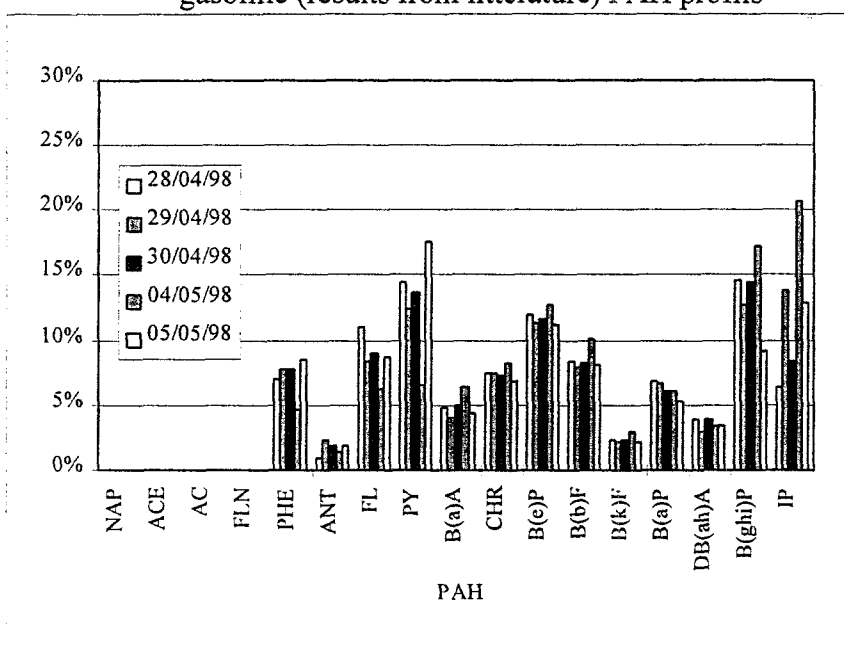


FIGURE 8. Profiles of PAH obtained in the Paris campaign.

Comparing the profiles of fig 7 with those of fig 8, a good correlation is observed, however, it can be noted that the contribution of both fuel types appears to be similar.

6. CONCLUSION

The analysis of each sample of diesel exhaust showed that besides PAH and oxygenated PAH, the organic fraction also contained n-alkanes and an unresolved complex mixture (UCM) of hydrocarbons. These compounds are characteristic of petroleum residues and vehicular exhaust.

PAH and oxygenated PAH were identified in both the gaseous and particulate phases and the results show the extent of the distribution between the two phases. In both the field and tunnel experiments it was observed that the PAH were predominantly found in the gaseous phase rather than in the particulate phase.

The work, therefore, highlights the importance of the sampling the gaseous phase, something which has been often neglected in previous studies.

Determination of the size distribution of diesel particles showed that the organic compounds were mainly adsorbed onto the very fine particulate fraction ($< 0.4 \mu\text{m}$). Particles of this size can reach the pulmonary alveoli carrying with them any adsorbed organics species such as PAH or oxygenated PAH.

In fact, oxygenated PAH were found to be present at greater concentrations than the PAH in the particulate phase. In the tunnel experiments up to 30 times more oxygenated PAH than PAH were found while the factor for ambient air was about 10. This factor is surely under estimated and very few toxicological data exist for these compounds. Given the high concentrations found, further studies are required for investigating these compounds in ambient air.

Finally, the field studies clearly show the contribution of traffic sources to the urban aerosol. However, the lack of supplementary information inhibits the possibility of recognising the exact contribution of diesel to urban aerosols. Nevertheless, the results observed show the same trends as those seen in the tunnel experiments with respect to the importance of sampling the gaseous phase for organics compounds as

well as the predominance of oxygenated PAH in the particulate phase.

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